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LTD:THE

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(54) RUBBER COMPOSITION

(57) Abstract:

PURPOSE: To obtain a rubber composition which is made directly bondable to a general-purpose rubber without detriment to high hardness inherent in a rubber composition comprising a hydrogenated ethylenically unsaturated nitrile/conjugated diene copolymer rubber, zinc methacrylate and an organic peroxide.

CONSTITUTION: This rubber composition comprises 100 pts.wt. nitrile copolymer composition comprising a nitrile copolymer (i) comprising a polymer chain

essentially consisting of an ethylenically unsaturated nitrile and a conjugated diene and having a conjugated diene unit content of 30wt.% or below, 10-100 pts.wt., per 100 pts.wt. (i), zinc salt (ii) of methacrylic acid and/or its derivative and a polybutadiene (BR) and/or a styrene/butadiene copolymer rubber (SBR) (iii) each of which has a 1,2-vinyl bond content of the butadiene part of 45wt.% or above and used in such an amount that the ratio of the total of (i) and (ii) to (iii) is 90/10 to 10/90 by weight, and 0.5-10 pts.wt. organic peroxide (iv).

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10 90 (i) nitrile copolymer: conjugated diene unit of 30wt% less 100 parts wt.
5 5 (ii) zinc salt of methacrylic acid. 10-100 parts wt.
90 10 (iii) polybutadiene or SBR.

20 carbon black

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LEGAL STATUS

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CLAIMS

[Claim(s)]

[Claim 1] (i) It consists of a polymer chain guided from ethylene nature unsaturated nitrile and conjugated diene at least. The nitril system copolymer rubber whose content of a conjugated diene unit is 30 or less % of the weight, (ii) The zinc salt of a methacrylic-acid and/or its derivative Per [10] (i) 100 weight section - the 100 weight sections, 1 of a butadiene (iii) part and the amount of 2-vinyl association in a list 45% of the weight or more of polybutadiene (BR), and/or styrene butadiene copolymer rubber (SBR) (i) And rubber constituent which comes to contain (iv) organic peroxide 0.5 - 10 weight sections to the nitril system copolymer constituent 100 weight section included at a rate that the weight ratio of total quantity/(iii) of (ii) is set to 90 / 10 - 10/90.

[Claim 2] The rubber constituent according to claim 1 whose content of the unsaturated nitrile unit of said nitril system copolymer rubber is 10 - 60 % of the weight per copolymer weight.

[Claim 3] Claim 1 which the zinc salt of said methacrylic acid or its derivative is 10 - 60 weight section in zinc-oxide conversion about 20 - 60 weight section and the (B) zinc compound in the (A) methacrylic acid or its derivative at methacrylic-acid conversion, and (A)/(B) and a (mole ratio) make react at a rate of 1 / 0.5 - 1/3, and obtain, or a rubber constituent given in 2.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the rubber constituent in which direct adhesion with a sulfur cross-linking diene system rubber constituent is possible by the high degree of hardness useful on the bead filler of a tire, a tread, a under tread, a side tread, etc. the various belts for power transfer, an industrial roll, etc.

[0002]

[Description of the Prior Art] The use in various fields for having the strength property which was [rate / of high elasticity / high intensity, the high degree of hardness,] excellent in various diene system rubber, especially hydrogenation acrylonitrile butadiene copolymer rubber (NBR) is expected.

[0003] For example, it is indicated that it is indicated that using together acrylic-acid zinc and sulfur to JP,63-22846,A at various diene system rubber is indicated, and it blends an acrylic-acid metal salt with diene system rubber at JP,63-241045,A, and it blends methacrylic-acid zinc with various rubber at JP,2-36246,A, and blending an acrylic-acid metal salt with diene system rubber is indicated by JP,2-206629,A. Furthermore, the rubber constituent for tire skid equipments which blended the zinc salt and organic peroxide of a methacrylic acid with Hydrogenation NBR etc. is indicated by JP,3-188138,A.

[0004] However, although these rubber constituents, especially the rubber constituent which blended the zinc salt and organic peroxide of a methacrylic acid with Hydrogenation NBR were excellent in mechanical characteristics, such as a degree of hardness, reinforcement, rigidity, and abrasion resistance, it cannot be pasted up general-purpose diene system rubber and directly. Therefore, using an IIR sheet and an ultra-high-molecular-weight-polyethylene sheet for the tire configuration rubber structure general-purpose in the layer of said hydrogenation NBR constituent as a glue line is proposed by JP,5-185805,A, for example. Furthermore, carrying out hardening vulcanization of the constituent containing said hydrogenation NBR constituent, acrylonitrile butadiene copolymer rubber, or isobutylene isoprene copolymer rubber, carrying out direct adhesion unification, and considering as rubber rubber adhesion complex is indicated by JP,5-186609,A.

[0005]

[Problem(s) to be Solved by the Invention] Therefore, this invention aims at offering the rubber constituent which can be pasted up general-purpose rubber especially diene system rubber, and directly, holding the high degree of hardness which is the property of the proper which the rubber constituent which consists of the zinc salt and organic peroxide of the ethylene nature unsaturated nitrile and conjugated diene copolymer rubber which were hydrogenated, and a methacrylic acid has.

[0006]

[Means for Solving the Problem] It consists of a polymer chain guided from ethylene nature unsaturated nitrile and conjugated diene at least. if this invention is followed -- (i) -- The nitril system copolymer rubber whose content of a conjugated diene unit is 30 or less % of the weight, (ii) The zinc salt of a methacrylic acid and/or its derivative Per [10] (i) 100 weight section - the 100 weight sections, 1 of a butadiene (iii) part and the amount of 2-vinyl association in a list 45% of the weight or more of

polybutadiene (BR), and/or styrene butadiene copolymer rubber (SBR) (i) And rubber constituent which comes to contain (iv) organic peroxide 0.5 - 10 weight sections to the nitril system copolymer constituent 100 weight section included at a rate that the weight ratio of total quantity/(iii) of (ii) is set to 90 / 10 - 10/90. It *****.

[0007] It is copolymer rubber which copolymerized ethylene nature unsaturated nitrile (for example, acrylonitrile, a methacrylonitrile, etc.) and conjugated dienes (for example, 1,3-butadiene, an isoprene, 1,3-pentadiene, etc.) according to the conventional method as said nitril system copolymer rubber blended with the rubber constituent concerning this invention. Or in order to reduce the content of a conjugated diene unit, you may be copolymer rubber which hydrogenated the conjugated diene unit. Furthermore, the copolymerization rubber which hydrogenated the conjugated diene unit in at least one sort of plural copolymers rubber and these copolymerization rubber, such as the monomer in which said ethylene nature unsaturated nitrile and conjugated diene, and copolymerization are possible, for example, a vinyl aromatic compound, unsaturated-carboxylic-acid ester, unsaturated-carboxylic-acid alkyl ester, unsaturated-carboxylic-acid alkoxy alkyl ester, and unsaturated-carboxylic-acid fluoro alkyl ester, can be mentioned.

[0008] The content of the unsaturated nitrile unit in a copolymer is desirable, at 10 - 60 % of the weight (still more preferably 15 - 55 % of the weight), the content of a conjugated diene unit is desirable and said nitril system copolymer is 30 or less (still more preferably 25 - 0 % of the weight) % of the weight. An unsaturated nitrile unit content is in the inclination for oilproof to get worse at less than 10 % of the weight, and when it exceeds 60 % of the weight conversely, the ductility in low temperature is lost and it is in the inclination which becomes easy to carry out a brittle fracture. Moreover, since weatherability will get worse if a conjugated diene unit exceeds 30 % of the weight, it is not desirable.

[0009] The polybutadiene (BR) and/or styrene butadiene copolymer rubber (SBR) which are blended as the second component of the rubber constituent concerning this invention If 1 of a butadiene part and the amount of 2-vinyl association remove that it is 50 - 80 % of the weight preferably 45% of the weight or more, BR or SBR (SBR obtained by any of an emulsion-polymerization method and a solution polymerization method is also included) of arbitration currently conventionally used widely as rubber can be used. In addition, since 1 of SBR or BR and the amount of 2-vinyl association become poor [a bridge formation adhesive property with a diene system rubber ingredient] at less than 45 % of the weight, it is not desirable. The loadings of SBR and/or BR are 10 / 90 - 90/10 in a weight ratio with the total quantity of the zinc salt (ii) of said nitril system copolymer rubber (i) and methacrylic acid, and/or its derivative, SBR, and/or BR (iii). Since bridge formation adhesion with a diene system rubber ingredient will become poor and dynamic-modulus E' will fall less than by 10/90 conversely if this weight ratio exceeds 90/10, it is not desirable.

[0010] the zinc salt of the methacrylic acid blended with the rubber constituent concerning this invention as the third component, or its derivative (for example, methacrylic acid) -- per [10] said nitril system copolymer rubber 100 weight section - the 100 weight sections -- 20-80 weight section combination is carried out preferably. these loadings -- this -- since original properties, such as said nitril system copolymer rubber, such as a degree of hardness, deteriorate if out of range, it is not desirable. The zinc salt of this methacrylic acid or its derivative can be obtained by making a methacrylic acid, or its derivative and zinc compound react out of a system or within a system. That is, it is 10 - 60 weight section in zinc-oxide conversion about 20 - 60 weight section and the (B) zinc compound at methacrylic-acid conversion, and (A)/(B) and a (mole ratio) can make the (A) methacrylic acid or its derivative able to react at a rate of 1 / 0.5 - 1/3, and the zinc salt of said methacrylic acid or its derivative can be obtained. said methacrylic acid or its derivative, and said zinc compound -- said -- since desired properties, such as a degree of hardness, deteriorate if out of range, it is not desirable. In addition, the / (B) ratio (aforementioned [A]) is the the best for making methacrylic-acid zinc generate during crosslinking reaction in a system. As said zinc compound, a zinc oxide, zinc carbonate, zinc hydroxide, etc. can be mentioned, for example.

[0011] The organic peroxide-blended as the fourth component of the rubber constituent of this invention
For example, the organic peroxide of the arbitration used for the peroxide vulcanization of usual rubber

can be used as indicated by JP 3-188138,A. For example, dicumyl peroxide, di-t-butyl peroxide, t-butyl cumyl peroxide, Benzoyl peroxide, 2, the 5-dimethyl -2, 5-(tert-butyl peroxide) hexyne - 3, 2, the 5-dimethyl -2, 5-JI (benzoylperoxy) hexane, One sort, such as 2, 5-dimethyl -2, 5-monochrome (tert-butyl peroxide) hexane, a, and a'-screw (tert-butyl peroxide-m-isopropyl) benzene, or more than it is mentioned. these organic peroxide -- per [0.5] said nitril system copolymer constituent 100 weight section - 10 weight sections -- 0.5-8 weight section combination is carried out preferably. In under the 0.5 weight section, since crosslinking density becomes small and sufficient reinforcement is not obtained, it is not desirable, and the loadings of said organic peroxide become [the elongation originally demanded as a rubber ingredient] small and are not desirable, if 10 weight sections are exceeded. [0012] the rubber constituent of this invention -- said indispensable component carried out -- in addition, the various additives currently generally used for the conventional rubber combination, such as an antioxidant, a bulking agent, a softener, a plasticizer, processing aid, and a joint use pons agent, can be blended, and this compound can be blended by the general approach and can be used as a product. The loadings of these additives can also be made into a general amount.

[0013]

[Example] It cannot be overemphasized that it is not what limits the range of this invention to these examples hereafter although an example explains this invention further.

[0014] Blended each component from the contents of combination (weight section) shown in examples 1-4 and the example 1 of a comparison - the 5 table I, and heat for 20 minutes, the bridge was made to construct at 160 degrees C, the test piece made into each purpose was prepared, various trials were performed by the following approach, and the physical properties were measured. The acquired physical properties are as being shown in Table I.

[0015] JIS degree of hardness: JIS K Based on 6301, it measured in 160 degrees-C x 20 minutes of cross-linking conditions.

[0016] Dynamic modulus: It measured using E' Oriental energy machine factory viscoelasticity spectrometer on 10% of static distortion, dynamic distortion of **2%, and the frequency of 20Hz.

[0017] Peel strength ASTM D The peel strength after vulcanization adhesion with the natural rubber basic compound ingredient of a publication was measured by the autograph to 3192-73. The configuration of a sample was a strip-of-paper-like sample with a width of face [of 25mm], and a die length of 15cm, after using one side as the rubber ingredient for evaluation, and the rubber ingredient of basic combination of another side and sticking them in the state of un-constructing a bridge, in 160 degree-Cx 20 minutes, constructed the bridge and was measured. Measurement of peel strength is JIS. K It carried out based on 6301.

[0018]

[Table 1]

表I

	比較例 1	比較例 2	比較例 3	実施例 1	実施例 2	実施例 3	比較例 4	実施例 4	比較例 5
SBR 1 ^{*1}	70	—	—	—	—	—	—	—	—
SBR 2 ^{*2}	—	70	—	—	—	—	—	—	—
SBR 3 ^{*3}	—	—	70	—	—	—	—	—	—
SBR 4 ^{*4}	—	—	—	70	—	—	—	—	—
SBR 5 ^{*5}	—	—	—	—	70	50	50	90	—
ニトリル系ゴム ^{*6}	30	30	30	30	30	50	—	10	100
天然ゴム ^{*7}	—	—	—	—	—	—	50	—	—
亜鉛粉	5	5	5	5	5	5	5	5	5
共架橋剤 ^{*8}	3	3	3	3	3	3	3	3	3
有機過酸化物 ^{*9}	3	3	3	3	3	3	3	3	3
合 計 (PHR)	111	111	111	111	111	111	111	111	111
JIS 硬度 架橋条件: 160°C×20分 BL, JIS=A, 温度=室温									
ピーク	76	87.4	88.8	95.6	98.2	98.4	77	96.2	96.6
伸張型粘弾性: E' ×10 ¹⁰ 架橋条件: 160°C×20分 20Hz, 10±2%, 幅=5mm									
MPa (60°C)	8.21	19.13	17.94	48.65	68.56	103.95	9.11	27.8	91.43
剥離強度 (Lab) 架橋条件: 160°C×20分 クロスヘッド=50mm, チャート=20mm									
剥離強度 (N/cm)	12	12	12	67	120	54	17	54	19
剥離形態 (破壊場所)	界面	界面	界面	ゴム相	ゴム相	ゴム相	界面	ゴム相	界面

* 1: St=18wt%, Vn=8.2wt%

* 2: St=15wt%, Vn=24.7wt%

* 3: St=25wt%, Vn=24.8wt%

* 4: St=20wt%, Vn=51.2wt%

* 5: St=14wt%, Vn=66.2wt%

* 6: 組成: 水素添加NBR組成物、結合ニトリル量=37%、水素添加率=89.8%
(共役ジエン単位=6.3重量%) 酸化亜鉛含有量=20重量部、
メタクリル酸含有量=20重量部

* 7: TTR 20 (Teck Bee Hang社製: Thailand)

* 8: トリメチロールプロパントリメタクリレート

* 9: 1,3-ビス-(*tert*-ブチルペルオキシ-イソプロピル) ベンゼン

[0019]

[Effect of the Invention] The constituent of the examples 1-4 according to this invention can obtain the rubber constituent excellent in the adhesive property with a rubber phase, without reducing a degree of hardness as compared with the example 5 (ZSC single taste) of a comparison so that clearly from the result of Table I and drawing 1.

[Translation done.]